⑫ EUROPEAN PATENT APPLICATION

㉞ Hollow Shaped catalytic extrudates.

㊗ The present invention relates to novel cross-section shapes which are employed to form catalytic extrudates which may be employed in catalytically promoted processes including hydrocarbon processing operations. Such shapes include essentially rectangular shaped tubes, and triangular shaped tubes in cross section.
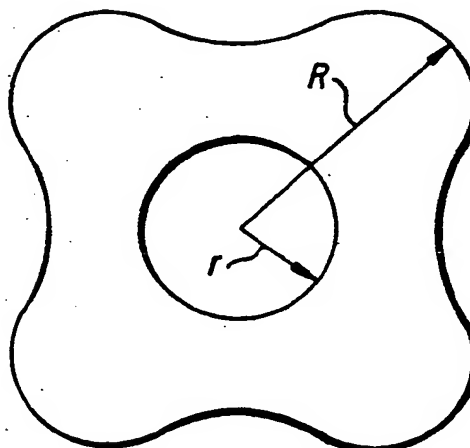
HOLLOW SHAPED CATALYTIC EXTRUDATES

The present invention relates to novel shaped formed particles which may be employed in a wide variety of catalytically activated and/or enhanced processes including, for example, alkylation or dealkylation of aryl compounds; the isomerization of various materials including, such as, xylene; and in the conversion of substances such as coal derived compounds or methanol or other hydrocarbons into materials such as olefins, fuels or lubricants. The particular configuration of the formed particles is selected to optimize the catalytic activity as well as physical properties such as pressure drop, crushing strength and abrasion resistance of the particle as well as the selectivity of the catalyst for the particularly desired product. The novel shaped formed particles of the present invention may also be employed for end use applications including guard bed service and/or as catalyst supports.

It has been known in the past that by selection of varied geometrical cross sectional configurations, formed catalytic particles may be designed to offer shorter diffusion paths for reactants and/or products which may be desirable in, for example, a diffusion controlled reaction. Additionally, catalytic particle configuration has been employed in the past to reduce the pressure drop encountered across a packed catalyst bed, and to reduce catalyst loss due to breakage, abrasion or crushing during handling, sizing or when severe process conditions are encountered. As a specific example, tubular extrudates have been employed in the past to improve the surface area-diffusion path presented by such catalytic particles, as well as to reduce the pressure drop encountered when reactants are passed through a catalytic bed. However, such tubular, cylindrical extrudates have the disadvantage of low crushing strength whereby during handling or use fracturing of the delicate tubular cylindrical structures results in fragmentation of the catalyst particle which will result in pressure drop increases in certain instances. The novel shapes of the present invention exhibit greater fracture resistance and, additionally, have a

reduced tendency toward end blockage by an adjacent particle in a randomly packed catalyst bed when compared to prior art tubular cylinder structures.

In accordance with one aspect of the present invention, novel tubular extrudate cross sectional configurations are provided which are specifically designed to reduce catalyst loss due to breakage, abrasion, or crushing forces which may be encountered in handling, sizing or severe process conditions. It has been shown in the past that by intentionally altering the shapes of formed particles from that most often utilized in fixed bed applications, i.e. a solid cylinder, the pressure drop or resistance to flow encountered across the bed can be reduced. In the case of formed catalytic particles, configurational changes so alter the surface-to-volume ratio that the resultant design offers shorter diffusion paths for reactants and/or products which may be desirable in, for example, a diffusion controlled catalytic reaction. Alternatively, changes in particle forms have been employed in the past to reduce loss due to breakage, abrasion or crushing during handling, sizing or when severe process conditions are encountered. As a specific example, the prior art discloses that tubular extrudates, for example formed particles possessing both cylindrical external perimeters and cylindrical internal cores or holes reduce the pressure drop across a packed bed of the same height relative to solid cylinders by virtue of the increase in bed void volume. Additionally in catalytic applications these tubular shaped entities have been employed to improve heat and mass transfer rates by virtue of their surface-to-volume enhancement, where such factors are controlling. However, such tubular, cylindrical extrudates have the disadvantage of low crushing strength relative to their solid counterparts. Consequentially, during handling or use fracturing of the delicate tubular cylindrical structures results in fragmentation of the particles which, in commercial applications, ultimately results in increased pressure drop as a result of an increase in resultant fines or dust. Conversely, the neoteric shapes of the present invention offer improvements in the resistance to fluid flow or pressure drop across a packed bed, and also

improvements in heat and mass trasfer properties as a consequence of
their favorable surface-to-volume ratios, which improvements are of
special significance in catalytic applications. In addition, and
entirely unexpected, the unique shapes herein below described,
simultaneously exhibit a resistance to loss due to breakage, abrasion
or crushing forces which may be encountered in handling, sizing or
under severe process conditions. Consequently, the extrudate shapes in
accordance with the present invention offer improvement over solid,
non-tubular, cross sections with respect to reduced pressure drop
across a fixed bed, and at least one or more of these shapes also
evidences a reduced tendency toward end blockage by an adjacent
particle in a ramdonly packed bed. Thus, by comparison to prior art
solid and tubular cylindrical structures, the packed bed pressure drop
advantage of these novel shapes is vastly superior.

For purposes of the present invention "tubular" is intended to
include configurations which in addition to hollow cylinders include
hollow or apertured structures having non-circular external perimeters,
e.g. rectangular, triangular or other geometrical configurations such
as multiple bulbous protrusions connected by concave surfaces specific
examples of which are shown in the accompanying Figures.

In accordance with the present invention catalyst particles
are provided having a centrally located aperture surrounded by a solid
wall portion, a volume-to-surface ratio of less than 0.51 mm (0.02
inch), and an external periphery characterized by having at least 3 and
no more than 4 points of contact when circumscribed by a cylindrical
shape.

Figure 1 is a photolithographic reproduction of a cross
section of a preferred form of catalyst particle in accordance with the
present invention.

Figure 2 is a photolithographic reproduction of a cross
section of another preferred form of catalyst particle in accordance
with the present invention.

Figure 3 is a photolithographic reproduction of a cross
section of still another preferred form of catalyst particle in
accordance with the present invention.

Figure 4 is a graphic representation of the specific embodiment of catalyst particle form as illustrated in Figure 1.

Figure 5 is a graphic representation of the catalyst particle form as illustrated in Figure 2.

Figure 6 is a graphic representation of the catalyst particle form as illustrated in Figure 3.

Figure 7 is a graphic representation of a cross-section of a prior art tubular cylindrical catalyst particle configuration.

The novel tubular catalyst extrudates in accordance with the present invention exhibit the following advantages:

(1)   Greater particle surface area per unit volume and shorter diffusion path for reactants and/or products.

(2)   Reduced pressure drop across a packed catalyst bed; and

(3)   Reduced catalyst loss due to breakage, abrasion, or crushing in handling, sizing, or under severe process conditions.

As hereinabove discussed, although the prior art cylindrical tube extrudates in some cases may exhibit advantages (1) and (2) noted hereinabove, they lack high crushing strength. The novel catalyst particle shapes in accordance with the present invention, by virtue of the increased number of points of-contact with one another, are able to radically alter the load distribution on a particle. Consequently, the novel shaped tubular catalytic extrudates of the present invention have been found to sustain crush or load per unit volume far greater than the prior art cylindrical tubular particle configurations.

It is known that certain reactions which require solid catalysts in the form of particles are limited by the rate of diffusion of the reactants into the particle and by the rate of the diffusion of the products formed by the reactants out of the particle. Accordingly, there is an advantage in making the particles so that they exhibit a high surface-to-volume ratio. This may be achieved by reducing the particle size. However, there is a practical lower limit to the size of the particle since as the particle size decreases the pressure drop required to pump the reactants through the catalyst bed increases. Also, prior art shapes are difficult to manufacture in diameters less

than 0.79 mm (1/32 inch) as well as their physical strength
characteristics being so poor as to be commercially unacceptable.

According to the present invention, there is provided a shaped
catalyst particle having an aperture formed through the central portion
thereof.

According to another preferred embodiment of the present
invention, there is provided a catalyst particle in a novel form which
has protrusions at the areas where its sides are joined together.
Further, the protrusions may be bulbous as in the case of the
configuration shown in Figure 1; or rounded as in the case of the
corners of the configurations shown in Figures 2 and 3. Although for
purposes of illustration these corners have been shown as being rounded
rather than pointed or sharp, it will be understood that such sharp
edges or corners have been rounded off, for example, to facilitate
manufacture and increase wear-resistance, but there may be instances
where sharp edges or corners are more desirable and accordingly are
included within the scope of the present invention.

It will be noted that particle configuration as shown in
Figures 1 and 4 is characterized by having bulbous protrusions around
the external periphery. It will be further noted that these
protrusions are continuous in that the areas between the individual
bulbs are continuously concave whereby each protrusion continuously
flows into an adjacent one in a smooth manner without any abrupt
discontinuity or pronounced angular-like interruptions.

The cross-sectional configuration of the catalyst particles
according to the present invention may be defined by means of a number
of various parameters. For example, r may be defined as the particle
aperture radius and R may be defined as the maximum distance from the
center of the aperture to the wall outer periphery. The wall thickness
will vary depending upon the particular tubular cross-section
configuration of the particle. In the case of the prior art
cylindrical tube configuration shown in Figure 7, assuming a uniformly
dimensioned hollow cylinder, R remains constant.

As shown in the accompanying Figures and drawings, R is the radius of a hypothetical cylinder which circumscribes the particle. The maximum thickness of the wall may vary in a ratio of R/r from 1.1 up to 10 and preferably from 1.5 to 5 and even more preferably from 2 to 3.

It will also be noted that there may be certain optimum wall thicknesses dependent upon the individual process applications. For example, in processes, which are significantly effected by heat and mass transfer, wall thickness on the order from 3,0 mm (1/8 inch) or less and preferably 2.5 mm (1/10 inch) or less and even more preferably 1.00 mm (1/25 inch) or less are preferable in such diffusion controlled reactions.

The novel catalyst particle configurations of the present invention are usefully employed in catalyst structures for heterogeneous reactions, for examples, support materials such as the difficultly reducible oxides of Groups II to IV of the Periodic Table including hydraulic cements, catalytically active oxides such as silica, alumina and oxides from Group V - VIII of the Periodic Table, and metals from Group IB and VIII of the Periodic Table. Catalysts are contemplated in the scope of the present invention which contain no added metal as well as catalysts which contain added metal. Metals such as, for example, nickel, platinum, silver, and the like. The catalyst particles of the present invention may comprise alumina or alumina as a support in admixture with a zeolite. Useful catalyst also include those containing cobalt and molybdenum oxides and copper and zinc oxides. The constituents may be all present at the time of shaping or may be practically added afterwards, for example, by impregnation.

As hereinbefore indicated, a wide variety of catalytic compositions may be employed utilizing the novel particle structures in accordance with the present invention including catalysts which comprise a crystalline allumino silicate zeolites. Such zeolites may have contained within their internal crystalline structure other materials such as, for example, amorphous silica, Fe_2O_3, B_2O_3, P_2O_5, and the like.

The crystalline zeolites which may be employed in accordance
with the present invention are members of a class of zeolitic materials
which exhibit unusual properties. Although these zeolites have
unusually low alumina contents, (high silica to alumina mole ratios),
they are very active even when the silica to alumina mole ratio exceeds
30. The activity is surprising since catalytic activity is generally
attributed to framework aluminum atoms and/or cations associated with
these aluminum atoms. These zeolites retain their crystallinity for
long periods in spite of the presence of steam at high temperature
which induces irreversible collapse of the framework of other zeolites,
such as that of X and A type. Furthermore, carbonaceous deposits, when
formed, may be removed by burning at higher than usual temperatures to
restore activity. These zeolites, used as catalysts, generally have
low coke-forming activity and therefore are conducive to long times on
stream between regenerations by burning carbonaceous deposits with
oxygen-containing gas such as air.

An important characteristic of the crystal structure of this
class of zeolites is that it provides a selective constrained access to
and egress from the intracrystalline free space by virtue of having an
effective pore size intermediate between the small pore Linde A and the
large pore Linde X. The pores of the structure are of about a size
such as would be provided by 10-membered rings of silicon atoms·
interconnected by oxygen atoms. It is to be understood, of course,
that these rings are those formed by the regular disposition of the
tetrahedra making up the anionic framework of the crystalline zeolite,
the oxygen atoms themselves being bonded to the silicon (or aluminum)
atoms at the centers of the tetrahedra.

The silica to alumina mole ratio referred to may be determined
by conventional analysis. This ratio is meant to represent, as closely
as possible, the ratio in the rigid anionic framework of the zeolite
crystal and to exclude aluminum in the binder or in cationic or other
form within the channels. Although zeolites with silica to alumina
mole ratios of at least 12 are useful, it is preferred in some
instances to use zeolites having substantially higher silica/alumina

ratios, e.g. 1600 and above. In addition, zeolites as otherwise characterized herein but which are substantially free of aluminum, that is zeolites having silica to alumina mole ratios of up to infinity, are found to be useful and even preferable in some instances. Such "high silica" or "highly siliceous" zeolites are intended to be included within this description. Also included within this definition are substantially pure silica analogs of the useful zeolites described herein, that is to say those zeolites having no measurable amount of aluminum (silica to alumina mole ratio of infinity) but which otherwise embody the chracteristics disclosed.

The novel class of zeolites, after activation, acquire an intracrystalline sorption capacity for normal hexane which is greater than that for water. This hydrophobic character can be used to advantage in some applications.

The novel class of zeolites useful herein have an effective pore size such as to freely sorb normal hexane. In addition, the structure must provide constrained access to larger molecules. It is sometimes possible to judge from a known crystal structure whether such constrained access exists. For example, if the only pore windows in a crystal are formed by 8-membered rings of silicon and aluminum atoms, then access by molecules of larger cross-section than normal hexane is excluded and the zeolite is not of the desired type. Windows of 10-membered rings are preferred, although in some instances excessive puckering of the rings or pore blockage may render these zeolites ineffective.

Although 12-membered rings in theory would not offer sufficient constraint to produce advantageous conversions, it is noted that the puckered 12-ring structure of TMA offretite does show some constrained access. Other 12-ring structures may exist which may be operative for other reasons and, therefore, it is not the present intention to entirely judge the usefulness of a particular zeolite solely from theoretical structural considerations.

Rather than attempt to judge from crystal structure whether or not a zeolite possesses the necessary constrained access to molecules

of larger cross-section than normal paraffins, a simple determination
of the "Constraint Index" as herein defined may be made by passing
continuously a mixture of an equal weight of normal hexane and
3-methylpentane over a sample of zeolite at atmospheric pressure
according to the following procedure. A sample of the zeolite, in the
form of pellets or extrudate, is crushed to a particle size about that
of coarse sand and mounted in a glass tube. Prior to testing, the
zeolite is treated with a stream of air at 540°C for at least 15
minutes. The zeolite is then flushed with helium and the temperature
is adjusted between 290°C and 510°C to give an overall conversion of
between 10% and 60%. The mixture of hydrocarbons is passed at 1 liquid
hourly space velocity (1 volume of liquid hydrocarbon per volume of
zeolite per hour) over the zeolite with a helium dilution to give a
helium to (total) hydrocarbon mole ratio of 4:1. After 20 minutes on
stream, a sample of the effluent is taken and analyzed, most
conveniently by gas chromatography, to determine the fraction remaining
unchanged for each of the two hydrocarbons.

While the above experimental procedure will enable one to
achieve the desired overall conversion of 10 to 60% for most zeolite
samples and represents preferred conditions, it may occasionally be
necessary to use somewhat more severe conditions for samples of very
low activity, such as those having an exceptionally high silica to
alumina mole ratio. In those instances, a temperature of up to 540°C
and a liquid hourly space velocity of less than one, such as 0.1 or
less, can be employed in order to achieve a minimum total conversion of
10%.

Also intended to be within the scope of the present invention
are zeolites such as zeolite X and Y; ZSM-Beta, mordenite and erionite.

The "Constraint Index" is calculated as follows:

Constraint Index =

$$\frac{\log_{10} \text{ (fraction of hexane remaining)}}{\log_{10} \text{ (fraction of 3-methylpentane remaining)}}$$

The Constraint Index approximates the ratio of the cracking rate constants for the two hydrocarbons. Zeolites suitable for the present invention are those having a Constraint Index of 1 to 12. Constraint Index (CI) values for some typical materials are:

|	C.I.
ZSM-4	0.5
ZSM-5	8.3
ZSM-11	8.7
ZSM-12	2
ZSM-23	9.1
ZSM-35	4.5
ZSM-38	2
ZSM-48	3.4
TMA Offretite	3.7
Clinoptilolite	3.4
Beta	0.6
H-Zeolon (mordenite)	0.4
REY	0.4
Amorphous Silica-Alumina	0.6
Erionite	38

The above-described Constraint Index is an important and even critical definition of those zeolites which are useful in the instant invention. The very nature of this parameter and the recited technique by which it is determined, however, admit of the possibility that a given zeolite can be tested under somewhat different conditions and thereby exhibit different Constraint Indices. Constraint Index seems to vary somewhat with severity of operation (conversion) and the presence or absence of binders. Likewise, other variables such as crystal size of the zeolite and the presence of occluded contaminants, may affect the constraint index. Therefore, it will be appreciated that it may be possible to so select test conditions as to establish more than one value in the range of 1 to 12 for the Constraint Index of a particular zeolite. Such a zeolite exhibits the constrained access as herein defined and is to be regarded as having a Constraint Index in the range of 1 to 12. Also contemplated herein as having a Constraint Index in the range of 1 to 12 and therefore within the scope of the defined novel class of highly siliceous zeolites are those zeolites which, when tested under two or more sets of conditions

within the above-specified ranges of temperature and conversion,
produce a value of the Constraint Index slightly less than 1, such as
0.9, or somewhat greater than 12, such as 14 or 15, with at least one
other value within the range of 1 to 12. Thus, it should be
understood that the Constraint Index value as used herein is an
inclusive rather than an exclusive value. That is, a crystalline
zeolite when identified by any combination of conditions within the
testing definition set forth herein as having a Constraint Index in
the range of 1 to 12 is intended to be included in the instant novel
zeolite definition whether or not the same identical zeolite, when
tested under other of the defined conditions, may give a Constraint
Index value outside of the range of 1 to 12.

The novel class of zeolites defined herein is exemplified by
ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-35, ZSM-38, ZSM-48, and other
similar materials.

ZSM-5 is described in greater detail in U.S. Patents No.
3,702,886 and Re 29,948. ZSM-11 is described in U.S. Patent No.
3,709,979. ZSM-12 is described in U.S. Patent No. 3,832,449. ZSM-23
is described in U.S. Patent No. 4,076,842. ZSM-35 is described in
U.S. Patent No. 4,016,245. ZSM-38 is more particularly described in
U.S. Patent No. 4,046,859.

ZSM-48 can be identified, in terms of moles of anhydrous
oxides per 100 moles of silica, as follows:
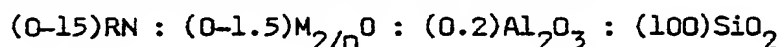
$$(0-15)RN : (0-1.5)M_{2/n}O : (0.2)Al_2O_3 : (100)SiO_2$$
wherein:

M is at least one cation having a
    valence n; and
RN is a C_1-C_{20} organic compound
    having at least one amine
    functional group of $pK_a < 7$.

It is recognized that, particularly when the composition
contains tetrahedral framework aluminum, a fraction of the amine
functional groups may be protonated. The doubly protonated form, in
conventional notation, would be $(RNH)_2O$ and is equivalent in
stoichiometry to 2 RN + H_2O.

The characteristic X-ray diffraction pattern of the synthetic
zeolite ZSM-48 has the following significant lines:

Characteristic Lines of ZSM-48

d (Angstroms)	Relative Intensity
11.9	W-S
10.2	W
7.2	W
5.9	W
4.2	VS
3.9	VS
3.6	W
2.85	W

These values were determined by standard techniques. The
radiation was the K-alpha doublet of copper, and a scintillation
counter spectrometer with a strip chart pen recorder was used. The
peak heights, I, and the positions as a function of 2 times theta,
where theta is the Bragg angle, were read from the spectrometer
chart. From these, the relative intensities, 100 I/I_0, where I_0
is the intensity of the strongest line or peak, and d (obs.), the
interplanar spacing in angstroms, corresponding to the recorded lines,
were calculated. In the foregoing table the relative intensities are
given in terms of the symbols W = weak, VS = very strong and W-S =
weak-to-strong. Ion exchange of the sodium ion with cations reveals
substantially the same pattern with some minor shifts in interplanar
spacing and variation in relative intensity. Other minor variations
can occur depending on the silicon to aluminum ratio of the particular
sample, as well as if it has been subjected to thermal treatment.

The ZSM-48 can be prepared from a reaction mixture containing
a source of silica, water, RN, an alkali metal oxide, such as sodium,
and optionally alumina. The reaction mixture should have a
composition, in terms of mole ratios of oxides, falling within the
following ranges:

REACTANTS		BROAD	PREFERRED
Al_2O_3/SiO_2	=	0 to 0.02	0 to 0.01
Na/SiO_2	=	0 to 2	0.1 to 1.0
RN/SiO_2	=	0.01 to 2.0	0.05 to 1.0
OH^-/SiO_2	=	0 to 0.25	0 to 0.1
H_2O/SiO_2	=	10 to 100	20 to 70
$H^+(added)SiO_2$	=	0 to 0.2	0 to 0.05

wherein RN is a C_1-C_{20} organic compound having amine functional group of $pK_a \leq 7$. The mixture is maintained at 80-250°C until crystals of the material are formed. $H^+(added)$ is moles acid added in excess of the moles of hydroxide added. In calculating $H^+(added)$ and OH values, the term acid (H^+) includes both hydronium ion, whether free or coordinated, and aluminum. Thus aluminum sulfate, for example, would be considered a mixture of aluminum oxide, sulfuric acid, and water. An amine hydrochloride would be a mixture of amine and HCl. In preparing the highly siliceous form of ZSM-48 no alumina is added. Thus, the only aluminum present occurs as an impurity in the reactants.

Preferably, crystallization is carried out under pressure in an autoclave or static bomb reactor, at 80°C to 250°C. Thereafter, the crystals are separated from the liquid and recovered. The compostion can be prepared utilizing materials which supply the appropriate oxide. Such compositions include sodium silicate, silica hydrosol, silica gel, silicic acid, RN, sodium hydroxide, sodium chloride, aluminum sulfate, sodium aluminate, aluminum oxide, or aluminum itself. RN is a C_1-C_{20} organic compound containing at least one amine functional group of $pK_a \leq 7$, as defined above, and includes such compounds as C_3-C_{18} primary, secondary, and tertiary amines, cyclic amine (such as piperdine, pyrrolidine and piperazine), and polyamines such as $NH_2-C_nH_{2n}-NH_2$ wherein n is 4-12.

The original cations can be subsequently replaced, at least in part, by calcination and/or ion exchange with another cation. Thus, the original cations are exchanged into a hydrogen or hydrogen ion precursor form or a form in which the original cation has been

replaced by a metal of Groups II through VIII of the Periodic Table.
Thus, for example, it is contemplated to exchange the original cations
with ammonium ions or with hydronium ions. Catalytically active forms
of these would include, in particular, hydrogen, rare earth metals,
aluminum, manganese and other metals of Groups II and VIII of the
Periodic Table.

It is to be understood that reference to the above-mentioned
patents to describe examples of specific members of the novel class
with greater particularity, it is intended that identification of the
therein disclosed crystalline zeolites be resolved on the basis of
their respective X-ray diffraction patterns. As discussed above, the
present invention contemplates utilization of such catalysts wherein
the mole ratio of silica to alumina is essentially unbounded. The
reference to the identified patents should therefore not be construed
as limiting the disclosed crystalline zeolites to those having the
specific silica-alumina mole ratios discussed therein, it now being
known that such zeolites may be substantially aluminum-free and yet,
having the same crystal structure as the disclosed materials, may be
useful or even preferred in some applications. It is the crystal
structure, as identified by the X-ray diffraction "fingerprint", which
establishes the identity of the specific crystalline zeolite material.

The specific zeolites described, when prepared in the
presence of organic cations, are substantially catalytically inactive,
possibly because the intra-crystalline free space is occupied by
organic cations from the forming solution. They may be activated by
heating in an inert atmosphere at 540°C for one hour, for example,
followed by base exchange with ammonium salts followed by calcination
at 540°C in air. The presence of organic cations in the forming
solution may not be absolutely essential to the formation of this type
zeolite; however, the presence of these cations does appear to favor
the formation of this special class of zeolite. More generally, it is
desirable to activate this type catalyst by base exchange with
ammonium salts followed by calcination in air at 540°C for from 15
minutes to 24 hours.

Natural zeolites may sometimes be converted to zeolite structures of the class herein identified by various activation procedures and other treatments such as base exchange, steaming, alumina extraction and calcination, alone or in combinations. Natural minerals which may be so treated include ferrierite, brewsterite, stilbite, dachiardite, epistilbite, heulandite, and clinoptilolite.

The preferred crystalline zeolites for utilization herein include ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-35, ZSM-38 and ZSM-48, with ZSM-5 being particularly preferred.

In a preferred aspect of this invention, the zeolites hereof are selected as those providing among other things a crystal framework density, in the dry hydrogen form, of not less than 1.6 grams per cubic centimeter. It has been found that zeolites which satisfy all three of the discussed criteria are most desired for several reasons. When hydrocarbon products or by-products are catalytically formed, for example, such zeolites tend to maximize the production of gasoline boiling range hydrocarbon products. Therefore, the preferred zeolites useful with respect to this invention are those having a Constraint Index as defined above of 1 to 12, a silica to alumina mole ratio of at least 12 and a dried crystal density of not less than 1.6 grams per cubic centimeter. The dry density for known structures may be calculated from the number of silicon plus aluminum atoms per 1000 cubic Angstroms, as given, for example, on page 19 of the article ZEOLITE STRUCTURE by W. M. Meier. This paper is included in PROCEEDINGS OF THE CONFERENCE ON MOLECULAR SIEVES, (London, April 1967) published by the Society of Chemical Industry, London, 1968.

When the crystal structure is unknown, the crystal framework density may be determined by classical pycnometer techniques. For example, it may be determined by immersing the dry hydrogen form of the zeolite in an organic solvent which is not sorbed by the crystal. Or, the crystal density may be determined by mercury porosimetry, since mercury will fill the interstices between crystals but will not penetrate the intracrystalline free space.

It is possible that the unusual sustained activity and stability of this special class of zeolites is associated with its high crystal anionic framework density of not less than 1.6 grams per cubic centimeter. This high density must necessarily be associated with a relatively small amount of free space within the crystal, which might be expected to result in more stable structures. This free space, however, is important as the locus of catalytic activity.

Crystal framework densities of some typical zeolites, including some which are not within the purview of this invention, are:

	Void Volume	Framework Density
Ferrierite	0.28 cc/cc	1.76 g/cc
Mordenite	.28	1.7
ZSM-5, -11	.29	1.79
ZSM-12	–	1.8
ZSM-23	–	2.0
Dachiardite	.32	1.72
L	.32	1.61
Clinoptilolite	.34	1.71
Laumontite	.34	1.77
ZSM-4 (Omega)	.38	1.65
Heulandite	.39	1.69
P	.41	1.57
Offretite	.40	1.55
Levynite	.40	1.54
Erionite	.35	1.51
Gmelinite	.44	1.46
Chabazite	.47	1.45
A	.5	1.3
Y	.48	1.27

When synthesized in the alkali metal form, the zeolite is conveniently converted to the hydrogen form, generally by intermediate formation of the ammonium form as a result of ammonium ion exchange and calcination of the ammonium form to yield the hydrogen form. In addition to the hydrogen form, other forms of the zeolite wherein the original alkali metal has been reduced to less than 1.5 percent by weight may be used. Thus, the original alkali metal of the zeolite may be replaced by ion exchange with other suitable metal cations of Groups I through VIII of the Periodic Table, including, by way of example, nickel, copper, zinc, palladium, calcium or rare earth metals.

In practicing a particularly desired chemical conversion
process, it may be useful to incorporate the above-described
crystalline zeolite with a matrix comprising another material resistant
to the temperature and other conditions employed in the process.   Such
matrix material is useful as a binder and imparts greater resistance to
the catalyst for the severe temperature, pressure and reactant feed
stream velocity conditions encountered in many cracking processes.

Useful matrix materials include both synthetic and naturally
occurring substances, as well as inorganic materials such as clay,
silica and/or metal oxides.   The latter may be either naturally
occurring or in the form of gelatinous precipitates or gels including
mixtures of silica and metal oxides.   Naturally occurring clays which
can be composited with the zeolite include those of the montmorillonite
and kaolin families, which families include the sub-bentonites and the
kaolins commonly known as Dixie, McNamee-Georgia and Florida clays or
others in which the main mineral constituent is halloysite, kaolinite,
dickite, nacrite or anauxite.   Such clays can be used in the raw state
as originally mined or initially subjected to calcination, acid
treatment or chemical modification.

In addition to the foregoing materials, the zeolites employed
herein may be composited with a porous matrix material, such as
alumina, silica-alumina, silica-magnesia, silica-zirconia,
silica-thoria, silica-beryllia, and silica-titania, as well as ternary
compositions, such as silica-alumina-thoria, silica-alumina-zirconia,
silica-alumina-magnesia and silica-magnesia-zirconia.   The matrix may
be in the form of a cogel.   The relative proportions of zeolite
component and inorganic oxide gel matrix, on an anhydrous basis, may
vary widely with the zeolite content ranging from between 1 to 99
percent by weight and more usually in the range of 5 to 80 percent by
weight of the dry composite.

EXAMPLE 1

The different catalyst shapes as illustrated in Figures 1
through 6 inclusive of the accompanying drawings and a cylindrical

tubular shape as illustrated in Figure 7 were extruded from the
following catalyst composition. The catalyst composition comprised
approximately 65% by weight of NaZSM-5 and 35% by weight of alumina.
More specifically aggregates of NaZSM-5 zeolite, 580.3g, (at 87.6%
solids) were mulled in a small batch mixer for 90 minutes to a fine,
uniform powder. To the zeolite, 368.7g (74.4% solids) of alpha
monohydrate alumina and 16g of a cellulose type extrusion aid were
added and the composition was mixed and mulled for 20 minutes.
Deionized water, 633.8g, was then slowly added to the mix, after which
mulling was continued for 60 minutes. By calculation the extrusion mix
contained 49% solids. The mix was then extruded at ambient temperature
by a hydraulic press. A die plate with the desired orifice
configuration was mounted on the outlet end of the extruder. It will
be obvious that the die plate orifice will determine the final
configuration of the shaped extrudate as illustrated in Figures 1, 2,
and 3. The catalyst mix was compacted and extruded out of the
respective die orifice. Following extrusion, the catalyst was dried
over night at 105°C - 121°C (220°F - 250°F) and stored.

    The size of the specific catalysts fabricated as well as their
crushing strengths, particle densities, and other physical
characteristics are described in the following Table 1.

TABLE 1

PHYSICAL PROPERTIES OF TUBULAR SHAPED EXTRUDATES

Reference	Cylindrical Tube	Fig. 1 Tube
Extrudate Wall Thickness,		
mm	0.99	0.30-0.99
in.	0.0390	0.0117-0.0390
Nominal Size (O.D.)		
mm	3.2	3.2
in.	0.125	0.125
Cross-sectional Area,		
mm^2	6.415	4.397
$in.^2$	0.009943	0.006816
Average Length,		
mm	Not measured	6.398
in.	Not measured	0.2519
Vp/Sp,		
mm	Not determined	0.315
in.	Not determined	0.01240
*Crush Strength,N/mm (lbs/in)		
Average	6.79 (38.8)	21.00 (119.9)
Range	3.85-10.2 (22-58)	14.-27.5 (80-157)
Crush Strength/Extrudate Volume		
kg/cm^3/(Tons/cu.in.)	108. (1.95)	487. (8.80)
Particle Density (mercury displacement)		
g/cc	0.855	0.848
**Pressure Drop Pa/m (in.H_2O/ft)		
(N_2 mass flow rate)		
47.88 kPa/hr (1000 lb/ft^2 hr)	–	7437 (9.1)
95.76 kPa/hr (2000 lb/ft^2 hr)	–	22884 (28.0)

*   In the Crushing Strength Test, a calcined extruded particle was placed on its side between two parallel, horizontal flat plates, one stationary and one movable. A gradually increasing force was applied to the movable plate perpendicular to the surface of the plate, until the particle broke. The crushing strength is the force in pounds applied at the instant particle breakage occurs. The crushing strength reported is the average value determined on 25 particles. The crushing test strength is related to the ability of the catalyst to withstand pressure drops and to support the catalyst bed in the reactor.

** For test description cf. Sabri Ergun, Anal. Chem. 23, 151 (1951)

TABLE 1 (cont.)
PHYSICAL PROPERTIES OF TUBULAR SHAPED EXTRUDATES

Reference	Fig. 2 Tube	Fig. 3 Tube
Extrudate Wall Thickness,		
mm	0.72-1.02	0.72-1.02
in.	0.0283-0.040	0.020-0.040
Nominal Size (O.D.)		
mm	3.2	3.2
in.	0.125	0.125
Cross-sectional Area,		
mm^2	4.988	4.021
$in.^2$	0.007732	0.006235
Average Length,		
mm	6.604	6.248
in.	0.260	0.246
Vp/Sp,		
mm	0.3632	0.295
in.	0.01439	0.0116
*Crush Strength,N/mm (lbs/in)		
Average	1.31 (74.8)	7.23 (41.3)
Range	6.83-22.6 (39-129)	3.85-14.4 (22-82)
Crush Strength/Extrudate Volume		
kg/cm^3/(Tons/cu.in.)	268. (4.85)	182. (3.29)
Particle Density (mercury displacement)		
g/cc	0.856	0.860
**Pressure Drop Pa/m (in.H_2O/ft)		
(N_2 mass flow rate)		
47.88 kPa/hr (1000 lb/ft^2 hr)	9154 (11.2)	10380 (12.7)
95.76 kPa/hr (2000 lb/ft^2 hr)	27543 (33.7)	29178 (35.7)

EXAMPLE 2

The different catalyst shapes as illustrated in Figures 1
through 6 inclusive of the accompanying drawings were extruded from the
following catalyst composition. The catalyst composition comprised
approximately 65% by weight of NaZSM-5B and 35% by weight of alumina.
More specifically aggregates of NaZSM-5 zeolite, 2450.5g, (at 88.3%
solids) were mulled in a small batch mixer for 30 minutes to a fine,
uniform powder. To the zeolite, 1642.7g (71.0% solids) of alpha
monohydrate alumina and 30g of a cellulose type extrusion aid were
added and the composition was mixed and mulled for 20 minutes.
Deionized water, 1876.8g, was then slowly added to the mix, after which

mulling was continued for 30 minutes. By calculation the extrusion mix
contained 55.5% solids. The mix was then extruded at ambient
temperature by an auger extruder. A die plate with the desired orifice
configuration was mounted on the outlet end of the extruder. It will
be obvious that the die plate orifice will determine the final
configuration of the shaped extrudate. The catalyst mix was extruded
out of the respective die orifice. Following extrusion, the catalyst
was dried over night at 105°C - 121°C (220°F - 250°F) and stored.

The size of the specific catalysts fabricated as well as their
crushing strengths, and particle densities, are described in the
following Table 2.

TABLE 2

PHYSICAL PROPERTIES OF TUBULAR SHAPED EXTRUDATES

Reference	Fig. 1 Tube	Fig. 2 Tube	Fig. 3 Tube
Extrudate Wall Thickness, mm/in.	0.30-0.99/0.0117-0.0390	0.72-0.12/0.0283-0.040	0.72-1.02/0.020-0.040
Nominal Size (O.D.) mm/in.	3.2/0.125	3.2/0.125	3.2/0.125
Cross-sectional Area, mm^2/in.^{2}	4.397/0.006816	4.988/0.007732	4.021/0.006235
*Crush Strength, N/mm (lbs/in.)			
Average	16.7 (95.1)	10.9 (62.3)	5.57 (31.8)
Range	9.6-28.0 (55-160)	7.2-20.7 (41-118)	3.32-10.9 (19-62)
Crush Strength/Extrudate Volume kg/cm^3 (Tons/cu. in.)	386 (6.98)	223 (4.03)	141 (2.55)
Particle Density (mercury displacement) g/cc	1.017	1.034	1.030

EXAMPLE 3

.   A catalyst with the shape as illustrated in Figure 1 of the
accompanying drawings and a catalyst with a cylindrical tubular shape
as illustrated in Figure 7 were extruded from the following catalyst
composition. The catalyst composition comprised approximately 65% by
weight of NaZSM-5 and 35% by weight of alumina. More specifically
aggregates of NaZSM-5 zeolite, 556.6g, (at 87.8% solids) were mulled in
a small batch mixer for 90 minutes to a fine, uniform powder. To the
zeolite, 353.7g (74.4% solids) of alpha monohydrate alumina and 16g of
a cellulose type extrusion aid were added and the composition was mixed
and mulled for 20 minutes. Deionized water, 673.7g, was then slowly
added to the mix, after which mulling was continued for 60 minutes. By
calculation the extrusion mix contained 47% solids. The mix was then
extruded at ambient temperature by a hydraulic press. A die plate with
the desired orifice configuration was mounted on the outlet end of the
extruder. Following extrusion, the catalyst was dried over night at
105°C - 121°C (220°F - 250°F) and stored.

The size of the specific catalysts fabricated as well as their
crushing strengths, densities, and other physical characteristics are
described in the following Table 3.

TABLE 3
PHYSICAL PROPERTIES OF TUBULAR SHAPED EXTRUDATES

Reference	Cylindrical Tube	Fig. 1 Tube
Extrudate Wall Thickness, mm/in.	0.99/0.0390	0.30-0.99/0.0117-0.0390
Nominal Size (O.D.) mm/in.	3.2/0.115	3.2/0.125
Cross-sectional Area, $mm^2/in.^2$	6.415/0.009943	4.397/0.006816
Average Length, mm/in.	7.05/0.2776	5.63/0.2215
Vp/Sp, mm/in.	0.434/0.0171	0.310/0.0122
*Crush Strength, N/mm/lbs/in.		
Average	3.15/18.0	15.4/88.1
Range	1.75-4.38/10-25	11.4-21.0/65-120
Crush Strength/Extrudate Volume		
kg/cm^3 (Tons/cu. in.)	50.4/0.91	358./6.46
Particle Density (mercury displacement)		
g/cc	0.841	0.861
**Pressure Drop, Pa/m (in. H_2O/ft)		
(N_2 mass flow rate)		
47.88 kPa/hr (1000 lb/ft^2 hr)	6702 (8.2)	8582 (10.5)
95.76 kPa/hr (2000 lb/ft^2 hr)	20514 (25.1)	26072 (31.9)

EXAMPLE 4

Conventional cylindrical shaped catalysts of three different sizes, i.e. 1.02 mm (1/25 inch), 1.59 mm (1/16 inch) and 3.2 mm (1/8 inch) diameter, were extruded from the following catalyst composition. The catalyst composition comprised approximately 65% by weight of NaZSM-5 and 35% by weight of alumina. More specifically, aggregates of NaZSM-5 zeolite (87.8% solids), 568.5g, were mulled in a small batch mixer for 90 minutes to a fine, uniform power. To the zeolite, 361.2g of alpha monohydrate alumina at 74.4% solids and 16g of a cellulose type extrusion aid were added and the composition was mixed and mulled for 20 minutes. Deionized water, 654.3g, was then slowly added to the mix, after which mulling was continued for 60 minutes. By calculation,

the extrusion mix contained 48% solids.   The mix was then extruded at
ambient temperature by a hydraulic press.   The formed catalyst was
dried over night at 105°C - 121°C (220-250°F) and stored.

The size of the specific catalysts fabricated as well as their
crushing strengths, particle densities and other physical
characteristics are described in Table 4.   The advantage of reduced
pressure drops of the novel shaped catalysts as illustrated in previous
examples becomes apparent when compared to 1.02 mm (1/25 inch) or 1.59
mm (1/16 inch) cylindrical shaped catalysts described in this example.

TABLE 4

PHYSICAL PROPERTIES OF CYLINDRICAL SHAPED EXTRUDATES

Reference	Cylinder	Cylinder	Cylinder
Nominal Size (O.D.) mm/in.	1.02/1/25	1.59/1/16	3.2/1/8
Cross-sectional Area, mm^2/in.^{2}	0.813/0.00126	1.72/0.00267	7.916/0.01227
Average Length, mm/in.	3.338/0.1314	4.646/0.1829	6.777/0.2668
Vp/Sp, mm/in.	0.215/0.00845	0.3192/0.01257	0.6292/0.02477
*Crush Strength, N/mm (lbs/in.)			
Average	0.403 (29.3)	7.02 (40.1)	8.39(47.9)
Range	2.8-7.9 (16-45)	4.4-9.8 (25-56)	4.7-12.6 (27-72)
Crush Strength/Extrudate Volume kg/cm^3 (Tons/cu. in.)	642. (11.6)	415. (7.5)	111. (2.0)
Particle Density (mercury displacement) g/cc	0.861	0.860	0.852
**Pressure Drop, Pa/m (in. H$_2$O/ft) (N$_2$ mass flow rate)			
47.88 kPa/hr (1000 lb/ft^2 hr)	32529. (39.8)	20187. (24.7)	8582. (10.5)
95.76 kPa/hr (2000 lb/ft^2 hr)	89004. (108.9)	58437. (71.5)	26235. (32.1)

EXAMPLE 5

        The different catalyst shapes as illustrated in Figures 2, 3
and 7 of the accompanying drawings were extruded from the following
catalyst composition. The catalyst composition comprised approximately
65% by weight of NaZSM-5 and 35% by weight of alumina. More
specifically aggregates of NaZSM-5 zeolite, 2207.6g, (at 88.3% solids)
were mulled in a small batch mixer for 30 minutes to a fine, uniform
powder. To the zeolite, 1479.9g (73.3% solids) of alpha monohydrate
alumina was added and the composition was mixed and mulled for 20
minutes. Deionized water, 2312.5g, was then slowly added to the mix,
after which mulling was continued for 30 minutes. By calculation the
extrusion mix contained 50.6% solids. The mix was then extruded at
ambient temperature by an auger extruder. A die plate with the desired
orifice configuration was mounted on the outlet end of the extruder.
It will be obvious that the die plate orifice will determine the final
configuration of the shaped extrudate. The catalyst mix was extruded
out of the respective die orifice. Following extrusion, the catalyst
was dried over night at 121°C (250°F) and stored.

        The size of the specific catalysts fabricated as well as their
crushing strengths, densities, and other physical characteristics are
described in the following Table 5.

EXAMPLE 6

        The 1.02 mm (1/25 inch) and 3.2 mm (1/8 inch) cylindrical
catalysts were extruded from the following catalyst composition. The
catalyst composition comprised approximately 65% by weight of NaZSM-5
and 35% by weight of alumina. More specifically aggregates of NaZSM-5
zeolite, 2229.5g, (at 88.3% solids) were mulled in a small batch mixer
for 30 minutes to a fine, uniform powder. To the zeolite, 1447.0g
(73.3% solids) of alpha monohydrate alumina was added and the
composition was mixed and mulled for 20 minutes. Deionized water,
2323.0g, was then slowly added to the mix, after which mulling was
continued for 30 minutes. By calculation the extrusion mix contained

50.5% solids. The mix was then extrudated at ambient temperature by an auger extruder. A die plate with the desired orifice configuration was mounted on the outlet end of the extruder. It will be obvious that the die plate orifice will determine the final configuration of the shaped extrudate. The catalyst mix was compacted and extruded out of the respective die orifice. Following extrusion, the catalyst was dried over night at 121°C (250°F) and stored.

The size of the specific catalysts fabricated as well as their crushing strengths, densities, and other physical characteristics are described in Table 5.

EXAMPLE 7

The 1.59 mm (1/16 inch) cylindrical catalyst and catalyst shaped as illustrated in Figure 1 were extruded from the following catalyst composition. The catalyst composition comprised approximately 65% by weight of NaZSM-5 and 35% by weight of alumina. More specifically aggregates of NaZSM-5 zeolite, 2207.6g, (at 88.3% solids) were mulled in a small batch mixer for 30 minutes to a fine, uniform powder. To the zeolite, 1432.7g (73.3% solids) of alpha monohydrate alumina and 15.0g of a cellulose type extrusion aid were added and the composition was mixed and mulled for 20 minutes. Deionized water, 2344.7g, was then slowly added to the mix, after which mulling was continued for 30 minutes. By calculation the extrusion mix contained 50% solids. The mix was then extrudated at ambient temperature by an auger extruder. A die plate with the desired orifice configuration was mounted on the outlet end of the extruder. It will be obvious that the die plate orefice will determine the final configuration of the shaped extrudate. The catalyst mix was compacted and extruded out of the respective die orifice. Following extrusion, the catalyst was dried over night at 121°C (250°F) and stored.

The size of the specific catalysts fabricated as well as their crushing strengths, densities, and other physical characteristics are described in Table 5.

TABLE 5 (Examples 5, 6, & 7)

PHYSICAL PROPERTIES OF TUBULAR SHAPED EXTRUDATES

Reference	Cylindrical Fig. 7 Tube	Fig. 1 Tube	Fig. 2 Tube	Fig. 3 Tube
Nominal Size (O.D.) mm(in.)	3.2 (1/8)	3.2 (1/8)	3.2 (1/8)	3.2 (1/8)
Cross-sectional Area, mm/in.^{2}	6.415/0.009943	4.397/0.006816	4.988/0.007732	4.023/0.006235
Average Length, mm/in.	5.18/0.204	6.32/0.249	5.23/0.206	5.64/0.222
Vp/Sp, mm/in.	0.541/0.0213	0.297/0.0117	0.340/0.0134	0.290/0.0114
*Crush Strength, N/mm (lbs/in.)				
Average	4.73 (27.0)	17.8 (101.9)	8.95 (51.1)	4.41 (25.2)
Range	2.98-6.30 (17-36)	11.4-22.4 (65-128)	5.6-13.7 (32-78)	2.98-6.83 (17-39)
Crush Strength/Extrudate Volume kg/cm^3 (Tons/cu. in.)	77.5 (1.4)	415. (7.5)	182 (3.3)	111. (2.0)
Particle Density (mercury displacement) g/cc	0.875	0.888	0.889	0.911
**Pressure Drop, Pa/m (in. H$_2$O/ft) (N$_2$ mass flow rate)				
47.88 kPa/hr (1000 lb/ft^2 hr)	9480. (11.6)	8827. (10.8)	10543 (12.9)	14384. (17.6)
95.76 kPa/hr (2000 lb/ft^2 hr)	27216. (33.3)	26317 (32.2)	30240 (37.0)	40456. (49.5)

TABLE 5 (Examples 5, 6, & 7) (cont.)

PHYSICAL PROPERTIES OF TUBULAR SHAPED EXTRUDATES

Reference	Solid 1/25" Cylinder	Solid 1/16" Cylinder	Solid 1/8" Cylinder
Nominal Size (O.D.) mm (In.)	1.02 (1/25)	1.59 (1/16)	3.2 (1/8)
Cross-sectional Area, mm/in.^{2}	0.8110/0.001257	1.979/0.003068	7.9174/0.012272
Average Length, mm/in.	4.65/0.183	5.18/0.204	6.05/0.238
Vp/Sp, mm/in.	0.229/0.0090	0.358/0.0141	0.617/0.0243
*Crush Strength, N/mm (lbs/In.) Average	8.25 (47.1)	9.63 (55.0)	11.3 (64.4)
Range	4.9-11.6 (28-66)	5.95-14.9 (34-85)	7.0-18.4 (40-105)
Crush Strength/Extrudate Volume kg/cm^3 (Tons/cu. In.)	1035 (18.7)	498 (9.0)	144 (2.6)
Particle Density (mercury displacement) g/cc	0.905	0.901	0.873
**Pressure Drop, Pa/m (in. H_2O/ft) (N_2 mass flow rate) 47.88 kPa/hr (1000 lb/ft^2 hr)	20024. (24.5)	16918. (20.7)	10053. (12.3)
95.76 kPa/hr (2000 lb/ft^2 hr)	53697. (65.7)	46831. (57.3)	29586. (36.2)

It is apparent from the data presented in the foregoing Tables that the novel shaped tubular extrudates in accordance with the present invention have vastly superior resistance to crushing forces when compared to the prior art cylindrical tube shaped extrudates.

As hereinbefore noted, the novel catalyst structures in accordance with the present invention may be employed in a variety of catalytically activated processes, as hereinabove described for example, hydroprocessing, dealkylation and alkylation including the alkylation of benzene, for example, the alkylation of benzene with ethylene to form ethylbenzene; processes such as the conversion of methanol to petrochemicals and gasoline; and isomerization processes such as, for example, xylene isomerization including vapor phase isomerization, high temperature isomerization, low pressure isomerization, de-ethylation isomerization and isomerization employing severe processing conditions. Included among the various processes which may be enhanced by employment of the catalyst structure of the present invention are processes such as dewaxing, isomerization, and the conversion of lower alkanols to petrochemicals and gasoline. Such processses are described in U.S. Patents Nos. 4,292,166; 4,247,921; 4,094,921; 4,239,996; and 4,138,440. In the following specific examples the catalyst structures of the present invention were employed, to illustrate the effectiveness of the present catalyst shapes in a benzene alkylation process and, more specifically an ethylbenzene process. The ethylbenzene process described hereinafter employs a solid, non-Friedel-Crafts catalyst to alkylate benzene with ethylene in contrast to other commercially known processes for the manufacture of ethylbenzene (the feedstock, for example, for styrene production, which employ Friedel-Crafts catalyst, most commonly, aluminum chloride in a mixed liquid-gas-phase reaction system.) A more detailed description of the alkylation process may be found in U.S. Patent Nos. 3,751,506 and 3,751,504.

EXAMPLE 8

A ZSM-5 containing catalyst of Figure 1 configuration was charged to a flow tubular reactor and the alkylation reaction was conducted at a total pressure of 2068 kPa (300 psig), WHSV of 4 grams of ethylene per gram of catalyst per hour and at a benzene/ethylene mole ratio of 10, and at a constant inlet temperature of 410°C (770°F). The conversion of ethylene at greater than 96.5% was maintained for 3 days. The diethylbenzene (DEB) to ethylbenzene (EB) ratio in the product increased from 0.071 to 0.073 over the course of the run.

Catalysts of other configurations were tested under similar reaction conditions. The ethylene conversion, the length of time at which it was maintained, and the diethylbenzene to ethylbenzene ratio in the product for all catalyst configurations are shown in the following Table 6. In the same table, typical physical properties of all catalyst configurations are also shown.

From the table, it is apparent that the catalyst configurations of the present invention have higher ethylene conversions, longer cycle time, lower diethylbenzene to ethylbenzene ratios, higher crushing strengths over the prior art, cylinderical tubular form and 3.2 mm (1/8 inch) cylinder. Although the catalytic activity on catalyst configurations of the present invention is approximately the same or slightly lower than that on 1.59 mm (1/16 inch) or 1.02 mm (1/25 inch) cylinder, the advantages of reduced pressure drop and high crushing strengths are realized.

TABLE 6

CATALYST CONFIGURATION	Fig. 1 Tube	Fig. 3 Tube	Cylindrical Tube
Catalytic Properties			
Ethylene Conversion %	96.5(min)	96(min)	95.1(min)
Length of time the conversion was maintained, days	3	4	1
DEB/EB Ratio	0.071-0.073	0.093-0.098	0.086
Typical Physical Properties of Catalyst Particles			
Vp/Sp, mm/in.	0.315/0.0124	0.295/0.0116	0.434/0.0171
Pressure Drop, Pa/m (in. H_2O/ft) (N_2 mass flow rate) 95.76 kPa/hr (2000 lb/ft^2 hr)	22884. (28)	29423. (36)	20433. (25)
Crushing Strength, N/mm (lbs/in.)	21.0 (120)	5.95 (34)	2.45 (14)

Reaction Conditions: 410°C (770°F) inlet temperature, 4 WHSV ethylene, Benzene/ethylene = 10/1 (mole), 2068 kPa (300 psig) total pressure.

TABLE 6 (cont.)

CATALYST CONFIGURATION	1/8" solid Cylinder	1/16" solid Cylinder	1/25" solid Cylinder
Catalytic Properties			
Ethylene Conversion %	91.4-88.6	97(min)	97.5(min)
Length of time the conversion was maintained, days	2	4	6
DEB/EB Ratio	0.09	0.080-0.085	0.060-0.069
Typical Physical Properties of Catalyst Particles			
Vp/Sp, mm/in.	0.6317/0.02487	0.320/0.0126	0.216/0.0085
Pressure Drop, Pa/m (in. H_2O/ft) (N_2 mass flow rate) 95.76 kPa/hr (2000 lb/ft^2 hr	26154. (32)	57211. (70)	89903. (110)
Crushing Strength, N/mm (lbs/in.)	10.5 (60)	8.76 (50)	5.25 (30)

Reaction Conditions: 410°C (770°F) inlet temperature, 4 WHSV ethylene, Benzene/ethylene = 10/1 (mole), 2068 kPa (300 psig) total pressure.

EXAMPLE 9

A NaZSM-5 containing catalyst of Figure 1 configuration was calcined in nitrogen, ammonia exchanged, and further calcined in air to yield the acidic HZSM-5 form. The catalyst was charged to a flow tubular reactor and the reaction of methanol (83% wt.) and H_2O (17% wt.) charge was conducted at a total pressure of 2068 kPa (300 psig), WHSV of 1.6 methanol, at a helium to methanol ractio of 9.1 to 1, and at a hot spot temperature of 413°C (776°F). Similarly, a HZSM-5 containing catalyst of 3.2 mm (1/8 inch) solid cylindrical configuration was tested. The product distribution of the two catalyst configurations is compared in Table 7. It can be seen that the novel shape of the catalyst of the present invention gave methanol conversion products which have ligher yields of gasoline range constituents, but lower yields of light gases than the prior art shape.

TABLE 7
REACTION OF METHANOL OVER HZSM-5 CATALYST

Particle Configuration	Figure 1 Tube	3.2 mm Solid Cylinder	Figure 1 Tube	3.2 mm Solid Cylinder
Temperature, °C	413	314	413	413
Time on Stream, hrs	20.0	20.5	68.0	92.8
Product Distribution Wt. %, HC				
C1	0.02	0.28	0.06	0.34
C2	0.17	0.55	0.27	0.34
C2=	0.11	0.67	0.50	2.36
C3	3.50	11.90	4.56	5.98
C3=	0.15	1.16	0.60	3.43
C to C3 subtotal	(3.95)	(14.56)	(5.99)	(12.45)
IC4	6.02	14.91	9.79	12.44
NC4	1.82	3.41	2.12	2.19
C4=	0.26	0.85	0.98	3.09
Total C4	(8.10)	(19.17)	(12.89)	(17.72)
IC5	9.62	7.92	10.82	9.72
NC5	1.06	0.79	1.18	1.00
C5=	0.34	0.22	0.88	1.08
C6 P+N	9.85	6.57	12.84	11.53
C6=	0.31	0.21	0.51	0.64
Benzene	0.69	0.35	0.46	0.31
C7 P+O+N	2.95	1.84	5.85	4.98
Toluene	5.86	3.27	3.54	2.02
C8 P+O+N	0.90	0.64	2.31	2.25
C8 A	16.68	11.74	11.53	9.04
C9 P+O+N+A	16.89	13.54	14.46	13.05
C10 P+O+N+A	10.92	7.19	6.04	3.36
Durene	9.65	10.43	9.10	9.64
C11-C12 P+O+N+A	0.63	0.32	0.98	0.75
Naphthalenes	1.37	1.15	0.47	0.36
C13 +'S	0.25	0.12	0.14	0.09
C5+ subtotal	(87.97)	(66.27)	(81.11)	(69.82)
Wt. % CH2 Conv.	100.00	100.00	100.00	100.00
HC recovery % theo.	91.47	106.58	96.52	107.96

Charge: 83 Wt. % CH$_3$OH, 17 Wt. % H$_2$O
2068 kPa, 1.60 WHSV CH$_3$OH, He/CH$_3$OH = 9.10
P-paraffins, O-Olefins, N-Naphthenes, A-aromatics

CLAIMS:

  1. A catalyst particle having a centrally located aperture
surrounded by a solid wall portion, a volume to surface ratio of less
than .51 mm (0.02 inch) and an external periphery characterized by
having at least 3 points of contact when circumscribed by a cylindrical
shape.

  2. A catalyst particle in accordance with Claim 1 having at
least 3 and no more than 4 points of contact when circumscribed by the
cylindrical shape.

  3. A particle in accordance with Claim 1 wherein the solid
wall portion has a thickness of R-r wherein R is the distance from the
center of the aperture to the external periphery and r is the radius of
the aperture, the particle being further characterized in that the
value of R/r may vary from 1.1 up to 10.

  4. A particle in accordance with Claim 1 wherein the external
periphery wall portion is in the form of an essentially rectangular
configuration.

  5. A particle in accordance with Claim 1 wherein the particle
external periphery is characterized by having at least one protuberance
and at least one concave surface.

  6. A particle in accordance with Claim 1 wherein the external
periphery is characterized by having an essentially triangle-like
configuration.

  7. A catalyst particle in accordance with any preceding Claim
wherein the particle is comprised of a member selected from the group
consisting of alumina, silica, aluminosilicates, and mixtures thereof.

  8. A catalyst particle in accordance with Claim 7 wherein the
particle comprises a zeolite.

  9. A catalyst particle in accordance with Claim 7 wherein the
particle comprises ZSM-5.

  10. A catalyst particle in accordance with any preceding
Claim wherein the particle comprises a mixture of a zeolite with a
member of the group consisting of alumina, silica, silica-alumina and
clay.

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11.   A process for the conversion of an organic charge which comprises contacting the same under conversion conditions with a catalyst comprising a crystalline aluminosilicate characterized by having a formed particle configuration comprising a centrally located aperture surrounded by a solid wall portion, a volume to surface ratio of less than 0.51 mm (0.02 inch) and an external periphery characterized by having at least 3 points of contact when circumscribed by a cylindrical shape.

12.   The process of Claim 11 wherein the crystalline aluminosilicate is a zeolite, the zeolite being characterized by a $SiO_2:Al_2O_3$ ratio of at least 5.

13.   The process of Claim 11 or 12 wherein the crystalline aluminosilicate zeolite is combined with a binder in an amount less than 90 weight percent, the binder being selected from the group comprising alumina, silica, clay and mixtures thereof.

14.   The process of Claim 11 wherein the charge comprises an oxygenate selected from the group consisting of methanol, ethanol, ether derivatives of lower alcohols and mixtures of alcohols and ethers.

15.   The process of Claim 14 wherein the methanol is converted to a product selected from the group comprising gasoline boiling range constituents and lower olefins.

16.   The process of Claim 15 wherein the conversion is selected from the group consisting of alkylation of an aromatic hydrocarbon, xylene isomerization, oligomerization of olefins, hydrocarbon cracking, toluene disproportionation and hydrodewaxing.

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FIG.1
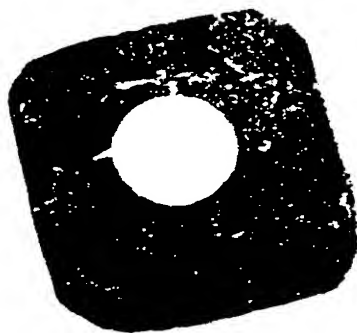
FIG.2
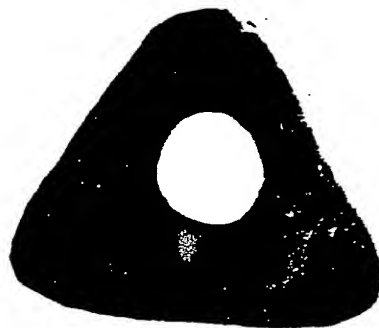
FIG.3
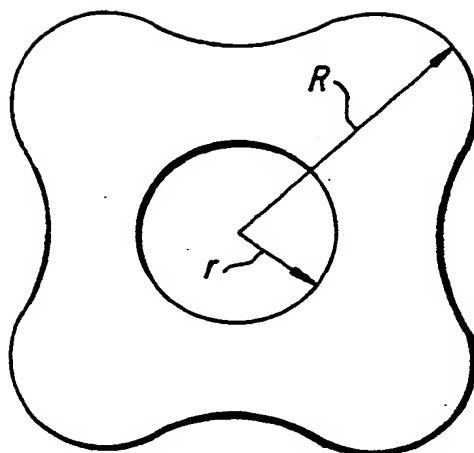
FIG. 4
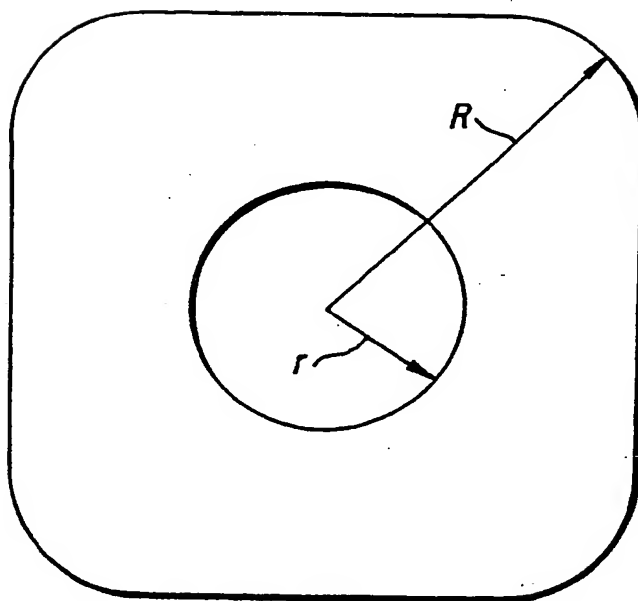
FIG. 5
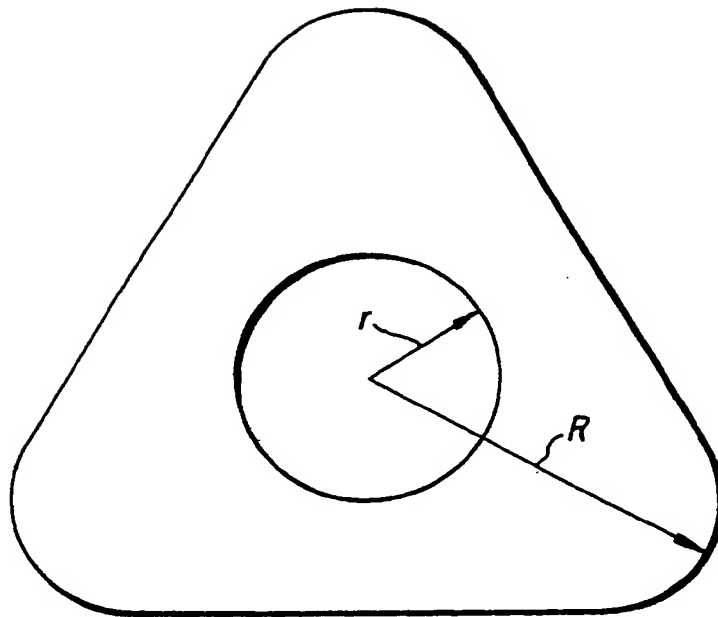
FIG. 6
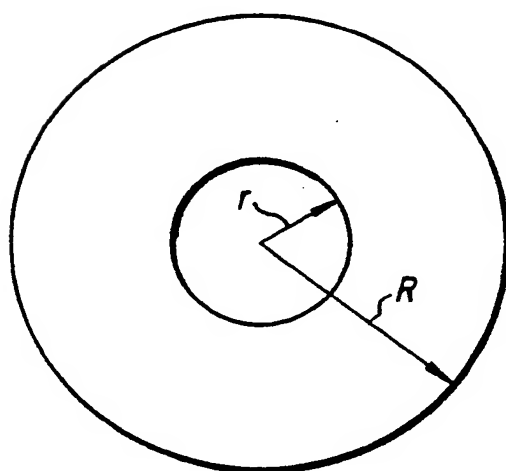
FIG. 7 PRIOR ART

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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
X	FR-A-2 365 625 (GULF) * Page 4, line 25 - page 6, line 27; page 8, line 27 - page 9, line 24; claims 1-14; figures *	1-11	B 01 J 35/04 C 10 G 3/00 C 10 G 11/05 C 10 G 45/64 C 07 C 1/20 C 07 C 5/27 C 07 C 6/12 C 07 C 2/66 C 07 C 2/12
Y	US-A-3 966 644 (W.R. GUSTAFSON) * Abstract; figures 5-11; column 3, line 37 - column 5, line 68; claims 1-7 *	1-13	
Y	BE-A- 886 363 (CAT. AND CHEM. EUROPE) * Pages 6-10; figures; claims 1-9 *	1-7	
Y	US-A-4 112 056 (N.Y. CHEN) * Abstract; column 2, lines 11-62; column 6, line 7 - column 8, line 61; claims 1-15 *	1-15	

TECHNICAL FIELDS SEARCHED (Int. Cl. ³)

Category	Citation		
A	US-A-4 328 130 (C.P. KYAN)		B 01 J C 10 G
A	EP-A-0 040 914 (MOBIL OIL)		
A	US-A-2 408 164 (A.L. FOSTER)		
A	US-A-2 644 800 (H.O. MOTTERN)		

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	01-09-1983	LO CONTE C.

European Patent Office

EUROPEAN SEARCH REPORT

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
D,A	US-A-3 709 979 (P. CHU)		

D,A	US-A-3 751 506 (G.T. BURRESS)		

D,A	US-A-4 292 166 (R.L. GORRING)		

TECHNICAL FIELDS SEARCHED (Int. Cl. ³)

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	01-09-1983	LO CONTE C.

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